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James Shaw-Stewart, Anna Alvarez-Reguera, Agata Greszta, James Marco, Maryam Masood, Rob Sommerville, Emma Kendrick

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James Shaw-Stewart[a], Anna Alvarez-Reguera[a], Agata Greszta[a], James Marco[a], Maryam Masood[a], Rob Sommerville[b], Emma Kendrick[a,b]

[a]WMG, University of Warwick, Coventry, UK, CV4 7AL
[b]College of Engineering and Physical Sciences, University of Birmingham, UK, B15 2TT

Email addresses: james@shawstewart.uk (James Shaw-Stewart),

e.kendrick@bham.ac.uk (Emma Kendrick)

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Abstract

The development of mass-market electric vehicles (EVs) using lithium-ion batteries (LIBs) is helping to propel growth in LIB usage, but end-of-life strategies for LIBs are not well developed. An important aspect of waste LIB processing is the stabilisation of such high energy-density devices, and energy discharge is an obvious way to achieve this. Salt-water electrochemical discharge is often mentioned as the initial step in many LIB recycling studies, but the details of the process itself have not often been mentioned. This study presents systematic discharge characteristics of different saline and basic solutions using identical, fully charged LIB cells. A total of 26 different ionic solutes with sodium (Na^+), potassium (K^+), and ammonium (NH_4^+) cations have been tested here using a fixed weight percentage concentration. An evaluation of possible reactions has also been carried out here. The results show good discharge for many of the salts, without significant damaging visual corrosion. The halide salts (Cl^-, Br^-, and I^-) show rapid corrosion of the positive terminal, as does sodium thiosulphate ($Na_2S_2O_3$), and the solution penetrates the cell can. Mildly acidic solutions do not appear to cause significant damage to the cell can. The most alkaline solutions (NaOH and K_3PO_4) appear to penetrate the cell without any clear visual damage at the terminals. Depending on what is desired by the discharge (i.e. complete cell destruction and stabilisation or potential re-use or materials recovery), discharge of individual Li-ion cells using aqueous solutions holds clear promise for scaled-up and safe industrial processes.

Keywords: batteries, solutes, stabilisation, electrolysis, safety, recycling

1. Introduction

Discharge of lithium-ion battery (LIB) cells is vital for stabilisation during LIB disposal in order to prevent explosions, fires, and toxic gas emission. These are consequences of short-circuiting and penetrating high-energy LIB devices, and can be hazardous to human health and the environment. Explosions, fires, and toxic gas emission may also damage disposal infrastructure, and damaged LIB materials could reduce the material value for recycling and materials reclamation. Indeed, when LIBs are accidentally entrained in lead-acid (Pb-acid) battery smelting input streams, fires

and explosions have been reported [1]. This highlights the risk that high-energy LIBs can pose during waste processing.

In the recently published text summarising the conclusions of the publicly-funded German LithoRec projects to develop a commercial LIB recycling process [2], there is a whole chapter devoted to safe discharge of LIBs [3]. This is needed for both safety and functional reasons, and Hauck and Kurrat [3] outline a number of discharge techniques for different scales, most are a set of different solid electronic techniques, plus the mention of conductive liquids like salt water. Unfortunately the use of conductive liquids is not discussed beyond NaCl (sodium chloride) solutions. The title of the chapter, "Overdischarging Lithium-Ion Batteries" reflects the authors assumption that *over*-discharging is necessary for materials reclamation. However, this assumption is not necessarily valid for keeping materials functional, and electrolytic potential windows in aqueous discharge allows a natural control on the minimum achievable discharge voltage.

This study was inspired by the large number of studies of disposal of lithium-ion batteries that involve salt-water discharge at the beginning [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. Despite this widespread usage and suggestions that it is a standard practice, there is little published information on the effectiveness of salt-water discharge. Before 2018, the only two examples from these articles are from Lu et al. [5] and Li et al. [13].

Lu et al. (2013) [5] varied the NaCl solution concentration between 1 %, 5 %, and 10 % for discharge of "new batteries, whose state of charge is about 60% and the voltage is about 3.85 V". Other than these initial electrical states, no further details were given about the LIBs, although the cathode chemistry is almost certainly lithium cobalt oxide (LCO) as that is the main objective of the study. A rapid drop in cell voltage is observed after as quickly as 7 minutes for the 10% NaCl solution which is attributed to "the leakage of case at the edge place". The method of voltage measurement is not made clear, but the rapid drop suggests an unrealistic drop in chemical potential energy, and that the measurement is a superficial one due to poor contact [5].

Li et al. (2016) [13] also varied the NaCl concentration between 0 %, 5 wt%, 10 wt%, and 20 wt%. They chose to measure the discharge via their own parameter, the "discharging efficiency", a function linearly linked to open circuit voltage. The cells were "18650... waste laptop batteries" with unspecified chemistries and initial voltage or state-of-charge (SOC). The results showed considerably slower discharge with NaCl in Li et al.'s study than for Lu et al.

Photos illustrated that corrosion happened for all cells, including apparently pure water, after 24 hours in the 30 ml solutions, and the metal concentrations in the residual solution were measured using ICP (inductively coupled plasma, without specifying elemental analysis technique). "High" levels of aluminium and iron were detected in all cases, and "medium" levels of cobalt, lithium, copper, calcium, and manganese were also measured. Significant quantities of zinc, barium and vanadium were also detected in all cases. All metals are assumed to have comed from the 18650 casings. Confirming the leakage of electrolyte, high concentrations of phosphorous were also measured alongside the corrosion residue, and not detected at all in the case of pure water discharge [13].

Highlighting the timely nature of this research into aqueous discharge are two 2018 publications by Li et al. [16] and Ojanen et al. [17]. Li et al. [16] was the first article that mentioned the use of a salt other than NaCl for cell discharge: sodium sulphate (Na_2SO_4). Ojanen et al. [17] attempts to take a systematic look at different salts as aqueous electrolytes in "electrochemical discharge": NaCl, $NaSO_4$ (*sic*), $FeSO_4$, and $ZnSO_4$, although the mechanism of discharge involved replacing a resistor for an electrochemical cell in a circuit rather than actually inserting the cell into the liquid solution.

The effects of water on batteries, particularly large packs, are also very important from a safety perspective, because of the hazards associated with hazardous-voltage (HV) EV packs a number of studies have been published on that topic in recent years [18, 19, 20]. Hoffman et al. [18] found that pure water was essentially benign in the two cases they looked at, with only very minor voltage drops, but they saw violent discharge in 3 % NaCl solutions, including significant heating of the water, but no fires were observed. Spek [19] looked at immersion of a number of full EVs, and saw a range of results from fire to no significant damage. Finally, Xu et al. [20] tried to examine failure mechanisms for HV battery packs, and concluded that electric arc caused by gas breakdown due to the severity of the electrolysis was likely to be the main factor in pack failures during water immersion. Xu et al. tested a range of NaCl concentrations up to 3.5 % (average sea water concentration), and gradually increased the voltage across two metal contacts until rapid failure occurred, due to arcing.

As exemplified above solution discharge is normally thought as synonymous for NaCl saline solution discharfe, which produces hydrogen and chlorine gas when electrolyzed as an aqueous solution [21]. However, NaCl is not an ideal solvent for discharge of batteries as chloride

ions accelerate aqueous corrosion of steel (and most metals).

In this study we have focussed on two principle considerations for aqueous solution discharge: the discharge rates and corrosion rates. Although optimisation would require a range of concentrations (particularly higher) for any given solute, we have kept to a single concentration (5 wt%) to make all solutes comparable, and used air conditioning to keep the room at ≈ 25 °C. Discharge has been measured at fixed time intervals up to 24 hours, and the terminal corrosion has also been visually observed at fixed time intervals up to 24 hours.

2.   Experimental

2.1.   *Cell characterisation*

In order to be as objective as possible in the evaluation of the salts the same type of 18650 LIB cell has been used throughout: the Sanyo UR18650RX - manufacturer's data is given in the supplementary information. A basic inventory of the relative weights of the components is shown in figure 1, from a single cell tear-down.

When discharging the cell, a very important energy aspect to characterise is the capacity as a function of voltage, which is shown in figure 2. The discharge capacity was measured directly using a slow C/50 (40mA) constant discharge down to zero V. The energy capacity was then calculated by integrating under a plot of voltage vs charge capacity.

Figure 2a depicts the incremental capacity (IC) to highlight the voltages at which more charge is available [22]. Two distinct IC peaks can be seen at 3.5 and 3.6 V, with largest falling around 3.6 V, in line with the nominal voltage specified by the manufacturer. Figure 2b depicts the energy capacity as a percentage of the maximum capacity, on a logarithmic scale. This helps to clarify the remaining percentage energy capacity at 1 to 3 V. The voltage as a function of energy is also shown with the axes reversed in figure 2c to further help visualise the remaining energy below 3 V. The cells were all tested using electrical impedance spectroscopy (EIS), charged up to 4.2 V, and weighed before the discharge experiments.

2.2.   *Electrolytes and discharge experiments*

A range of aqueous electrolyte solutions were made, all to 5 wt% concentration, using the salts outlined in table 1 (except for NaOH and NH_3 which are bases). The solutes were all over 95 %

purity, most over 99 %, and were purchased from various commercial chemical suppliers. The solutes were chosen for various reasons, but because feasibility studies showed that corrosion was primarily located on the positive electrode for NaCl solutions, this study focuses on varying the anions. Nevertheless alternative cations from Na^+ were also chosen, with K^+ picked for the greater dissociation than sodium, and because some salts with certain halide anions were cheaper. NH_4^+ was chosen to compare a common 'weak base' cation with the sodium and potassium, which both form strong bases.

Table 1: All 26 solutes used in this study.

Na$^+$ Solutes	K$^+$ Solutes	NH$_4^+$ Solutes
NaCl	KCl	
NaHSO$_4$	KBr	
Na$_2$SO$_4$	KI	(NH$_4$)$_2$SO$_4$
Na$_2$S$_2$O$_3$		
NaNO$_2$		
NaNO$_3$		
Na$_2$CO$_3$	K2CO$_3$	(NH$_4$)$_2$CO$_3$
NaHCO$_3$	KHCO$_3$	NH$_4$HCO$_3$
NaOH	K$_3$PO$_4$	NH$_3$
Na$_2$HPO$_4$	K$_2$HPO$_4$	(NH$_4$)$_2$HPO$_4$
NaH$_2$PO$_4$	KH$_2$PO$_4$	NH$_4$H$_2$PO$_4$
Na$_3$C$_6$H$_5$O$_7$		

The solutions were all made in two litre plastic bottles in at least the first instance, the large volume chosen to help keep temperatures more even, both for experimental quality and reproducibility, but also to potentially improve safety. For subsequent tests one litre plastic bottles were used. All the experiments were carried out in a well-ventilated, controlled climate of 25 °C, and the temperature was measured in at least one solution on-line throughout the experiments, which showed that the solution temperature was generally 22-23 °C.

The official hazard statements are all shown in table 2, and given that hazards need to be kept to a minimum for brine discharge to be competitive with resistive discharge, where safety is paramount, less hazardous salts are clearly more attractive. Table 2 shows that NaOH, NaNO$_2$,

K_2CO_3, and NH_3 have three official hazard statements, whilst $NaNO_3$ and K_3PO_4 both have two hazard statements. $NaHSO_4$, Na_2CO_3, KBr, $(NH_4)_2CO_3$, NH_4HCO_3 all have one hazard statement, leaving 15 hazard-free salts. Obviously, these official hazards do not take into account any effects from chemical contamination by electrolytic products and corrosion of the cell terminals.

In all cases the pH, conductivity and specific gravity of the brine solutions was measured before and after discharge. The pH was measured using an Oakten EcoTestr pH 2 handheld device, and the conductivity was measured using an Oakten COND 6+. The specific gravity was measured using a variety of analogue hydrometers. In some cases the salt ions may be consumed in the electrolysis, but in most cases it is believed that the salts act as non-consumed electrolytes, with the water electrolysing at both electrodes to generate hydrogen and oxygen. See section 3 for details on the possible products of theoretical competing reactions.

Table 2: Official hazard statements for the solutes used.

Hazard	Description	Salts
H272	H272	$NaNO_2$, $NaNO_3$
H290	H290	$NaOH$
H301	H301	$NaNO_2$
H302	H302	$(NH_4)_2CO_3$, NH_4HCO_3
H314	H314	$NaOH$, NH_3
H315	H315	K_2CO_3
H318	H318	$NaOH$, $NaHSO_4$, K_3PO_4
H319	H319	$NaNO_3$, Na_2CO_3, KBr, K_2CO_3
H335	H335	K_2CO_3, K_3PO_4, NH_3
H400	H400	$NaNO_2$, NH_3

The cells were charged up to 4.2 V (100% SOC), and dropped into the brine baths to start discharge. For each of the salts at least one discharge experiment was carried out where the cells were dropped into the bath with no connections, and removed at 30 minute intervals, for 10 hours, to manually measure the cell voltage using a handheld multimeter (Rapid RHMM17). These results were used for the main comparison as the contamination risk is kept to a minimum. The cells were then left to complete discharging overnight before being finally removed 24 hours after starting the discharge.

At 5, 10, and 24 hours the cells were all taken out of the solutions to observe the corrosion visually, and photographed using a digital camera.

2.3. *Post-discharge analysis*

After 24 hours of discharge the liquid properties of specific gravity, pH, and conductivity were measured to compare with the values before immersing the cell in the solutions. As well as photographs and cell voltage, the weight of the cells was measured. This was also measured two weeks later to allow the volatile solvents to evaporate off.

Where the electrodes were not completely corroded, electrical impedance spectroscopy (EIS) measurements were carried out using a BioLogic VMP3 multi potentiostat, with BH-1i cell holders. These results were compared to a single cell discharged via resistors, at various states of charge. The EIS measurements were taken over a range of frequencies from 100 kHz down to 1 mHz, with 10 mV amplitude and nine measurements per logarithmic decade.
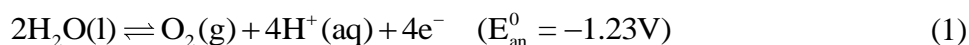
3   Theoretical electrolytic reactions

The standard cell potential for water dissociation (E_{cell}^0) and the corresponding anodic (E_a^0) and cathodic (E_c^0) $\frac{1}{2}$ cell reactions are shown in equations 1 to 6. All of the following redox reactions and potentials are derived from the CRC Handbook of Chemistry and Physic' chapter entitled "Electrochemical Series" [23], and half-cell potentials are all relative to a standard hydrogen electrode (SHE).
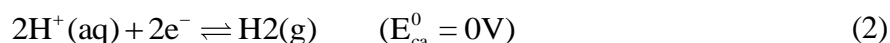
At the cell's negative terminal (cathode for aqueous solute electrochemical reactions), the vast majority of the solutes, particularly the Na^+ and K^+ ones, evolve hydrogen gas according to equations 5 or 2 depending on the pH of the solution and the balancing equation at the other electrode. For water reduction at the positive battery terminal (anode), equations 4 and 1 are the balancing equations, generating both oxygen gas and electrons for the completion of the circuit, and the potential given is the oxidation potential (-ve of the reduction potential).
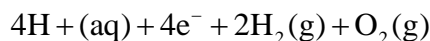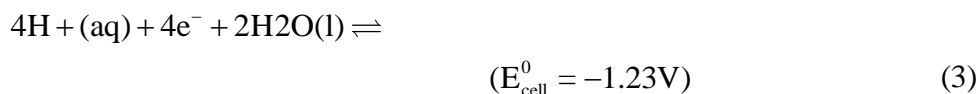
In acidic solutions:

Anode (oxidation):

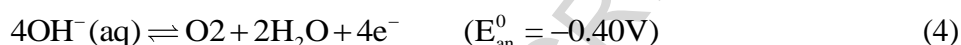$$2H_2O(l) \rightleftharpoons O_2(g) + 4H^+(aq) + 4e^- \quad (E_{an}^0 = -1.23V) \tag{1}$$

Cathode (reduction):

$$2H^+(aq) + 2e^- \rightleftharpoons H2(g) \qquad (E^0_{ca} = 0V) \qquad (2)$$

The total equation in acidic media is:

$$4H + (aq) + 4e^- + 2H2O(l) \rightleftharpoons$$

$$(E^0_{cell} = -1.23V) \qquad (3)$$

$$4H + (aq) + 4e^- + 2H_2(g) + O_2(g)$$

In alkali solutions:

Anode (oxidation):

$$4OH^-(aq) \rightleftharpoons O2 + 2H_2O + 4e^- \qquad (E^0_{an} = -0.40V) \qquad (4)$$

Cathode (reduction):

$$H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \qquad (E^0_{ca} = -0.83V) \qquad (5)$$

The total equation in alkali media:

$$4OH^-(aq) + 4e^- + 2H_2O(l) \rightleftharpoons$$

$$(E^0_{cell} = -1.23V) \qquad (6)$$

$$4OH^-(aq) + 4e^- + 2H_2(g) + O_2(g)$$
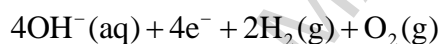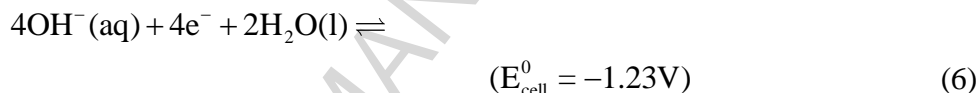
The cell potential for water dissociation is -1.23~V and can proceed via a basic or acidic reaction route. Applying a voltage of above 1.23~V will cause water electrolysis, however there are kinetic barriers that manifest themselves as overpotentials for each half-cell reaction [24]. The faster the ions move through solutions the quicker the discharge of the cell, until equilibrium of the components is reached. If gases are lost then the equilibrium will not occur according to Le Chatelier's principle.
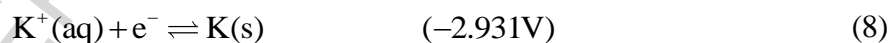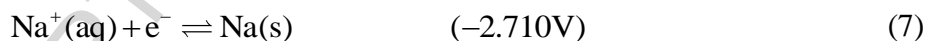
3.1. Competing cathodic reactions

In practice, at the negative terminal the cation may typically be looked at as providing a competing reduction reaction to water reduction (equations 2 and 5), but the anions do also demonstrate some capability in this area.

Table 3: A comparison of cathodic half-reactions competing with hydrogen generation from water electrolysis at the negative terminal of the cell, with the total theoretical potential difference given in acidic or basic aqueous solutions undergoing water electrolysis at the other (positive) terminal.

	Cathodic half equation	E_{ca}^0 vs SHE (V)	Acidic E_{cell}^0 (V) (-1.23)	Basic E_{cell}^0 (V) (-0.40)
(7)	$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71	-3.93	-3.10
(8)	$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93	-4.16	-3.33
(9)	$2NH_4^+(aq) + 2e^- \rightleftharpoons H_2(g) + NH_3(g)$	$\geq$ -0.83	$\geq$ -2.06	$\geq$ -1.23
(10)	$NO_3-(aq) + 2H^+(aq) + e^- \rightleftharpoons NO_2(g) + H_2O(l)$	+0.80	-0.43	n/a
(11)	$NO_3^- + 4H^+ + 2e^- \rightleftharpoons NO + 2H_2O$	+0.96	-0.27	n/a
(12)	$NO_2-(aq) + 2OH-(aq) \rightleftharpoons NO_3-(aq) + H_2O(l) + 2e^-$	-0.01	n/a	-0.39
(13)	$2NO_2^- + 3H_2O + 4e^- \rightleftharpoons N_2O + 6OH$	+0.15	n/a	-0.25
(14)	$PO_4^{3-}(aq) + 2H_2O(l) + 2e^- \rightleftharpoons HPO_3^{2-}(aq) + 3OH-(aq)$	-1.05	n/a	-1.45

Na^+ and K^+ generally demonstrate no variation from the standard quantities of gas production because Na and K metal deposition does not compete with H2 generation as demonstrated by the large negative reduction potentials in equations 7 and 8. The total cell reactions versus water oxidation are shown in table 3 where it can be seen that the most positive total potential difference (E_{cell}^0) is -3.10 V, far below the water potential of -1.23 V.

$$Na^+(aq) + e^- \rightleftharpoons Na(s) \qquad (-2.710V) \qquad (7)$$

$$K^+(aq) + e^- \rightleftharpoons K(s) \qquad (-2.931V) \qquad (8)$$

$$2NH_4^+(aq) + 2e^- \rightleftharpoons H_2(g) + NH_3(g) \qquad (?V) \qquad (9)$$

The electrolysis of ammonium ions at the cathode could in theory happen according to equation 9, but the only aqueous example that could be found in literature comes from metal plating by Berkh et al. who observed the onset of hydrogen production with $(NH_4)_2SO_4$ at a more positive potential relative to pure H_2O [25]. This suggests that the reduction potential of ammonium is likely to be non-competitive with that of water (and therefore considerably above at least -0.83 V vs SHE), which would explain why ammonia electrolysis studies assume the water provides the hydrogen, and focus on ammonia oxidation to aid hydrogen generation [26], which may be an incorrect assumption.

The main other potential competing cathodic reactions, identified in the CRC Handbook of Chemistry and Phsyics' chapter on Electrochemical Series, are for nitrates (equations 10 and 11) and nitrites (equations 12 13), with phosphates also potentially competitive in basic solutions (equation 14) [23].

$$NO_3 - (aq) + 2H^+(aq) + e^-$$
$$\rightleftharpoons NO_2(g) + H_2O(l) \qquad (+0.80V) \qquad (10)$$

$$NO_3 - (ag) + 4H^+(aq) + 2e^-$$
$$\rightleftharpoons NO(g) + 2H2O(l) \qquad (+0.96V) \qquad (11)$$

$$NO_2 - (aq) + 2OH - (aq)$$
$$\rightleftharpoons NO_3 - (aq) + H_2O(l) + 2e^- \qquad (-0.01V) \qquad (12)$$

$$2NO_2 - (aq) + 3H_2O(l) + 4e^-$$
$$\rightleftharpoons N_2O(g) + 6OH - (aq) \qquad (+0.15V) \qquad (13)$$

$$PO_4^{3-}(aq) + 2H_2O(l) + 2e-$$
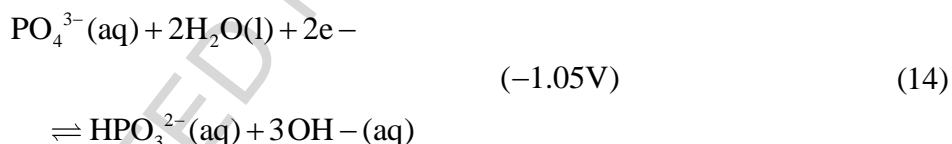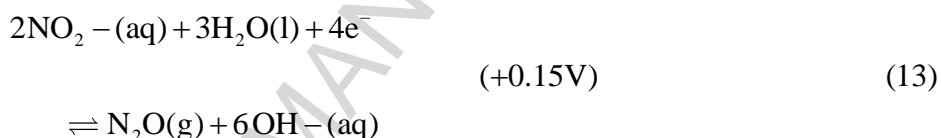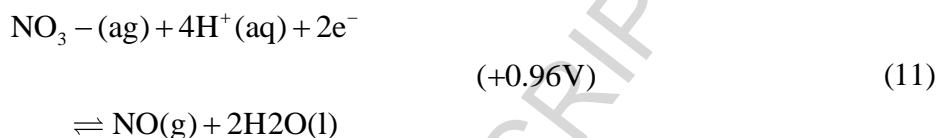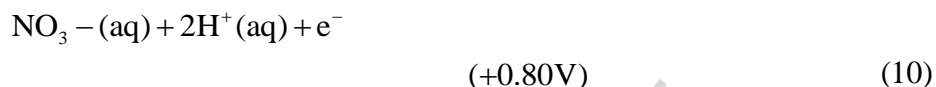$$\rightleftharpoons HPO_3^{2-}(aq) + 3OH - (aq) \qquad (-1.05V) \qquad (14)$$

Table 3 gives a good overview of the possible competing cathodic reactions at the negative electrode, and the total E_{cell}^0 for each of these with water electrolysing to generate oxygen at the anode (positive terminal). As all of the anionic reduction reactions involve H^+ or OH^- species, they are expected to occur significantly only in acidic or basic solutions, respectively. Both nitrate half-equations involve H^+ ions, and are at significantly higher potentials than water reduction, meaning they would dominate in acidic environments, producing preferentially NO_2 in the case of equation 11 at a potential 0.16 V higher than the production of NO in the case of equation 10. Since they are both competitive with each other, a mix of both gases may be expected to be produced, but both are significantly toxic, and often referred to as NO_x.

The two competing cathodic reduction reactions for nitrites (equations 12 13) both involve OH^- ions which suggest they will only occur in basic solutions, and again have significantly higher reduction potentials than water reduction in basic solutions (equation 5). Equation 13, with the

highest half-cell potential of + 0.15 V, also produces a nitrogen oxide, N_2O, otherwise known as nitrous oxide/laughing gas. N_2O is far less toxic than NO_x for the environment, less flammable, and less dangerous to human health.

The final competing reaction is for phosphate ions in equation 14. It involves OH^- ions and so will only occur in basic solutions, although the potential is significantly lower than for nitrites, and is actually lower than water reduction in equation 5, meaning that although it may compete with water reduction, hydrogen production should still dominate.
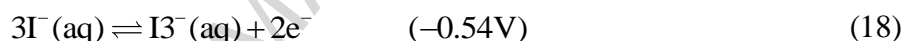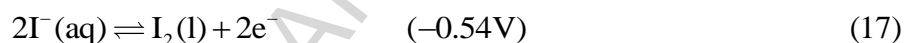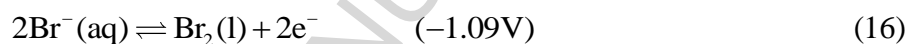
3.2. *Competing anodic reactions*

For the halides, the competing reactions appear to be relatively competitive (eqns 15-18), although it would appear that chlorine oxidation to chlorine gas (Cl_2 requires a larger potential than oxygen evolution in both acidic and basic solutions, but they are close enough in acidic solutions (only 0.13 V more positive) to mean that significant quantities of both can be generated. Table 4 shows that the E_{cell}^0 for halide reduction in acidic media is more competitive with water electrolysis than in an alkaline (basic) solution because the acidic reduction potential of water in equation 2 is more positive than the basic reduction potential of water in equation 5.
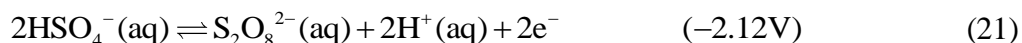
Table 4: A comparison of anodic half-reactions competing with oxygen generation from water electrolysis at the positive terminal of the cell, with the total theoretical potential difference given in acidic or basic aqueous solutions undergoing water electrolysis at the other (negative) terminal.

		Anodic half equation	E_{an}^0 vs SHE (V)	Acidic E_{cell}^0 (V) (0.00)	Basic E_{an}^0 (V) (-0.83)
(15)		$2Cl^-(aq) \rightleftharpoons Cl_2(g) + 2e^-$	-1.36	-1.36	-2.19
(16)		$2Br^-(aq) \rightleftharpoons Br_2(l) + 2e^-$	-1.09	-1.09	-1.92
(17)		$2I^-(aq) \rightleftharpoons I_2(l) + 2e^-$	-0.54	-0.54	-1.36
(18)		$3I^-(aq) \rightleftharpoons I_3^-(aq) + 2e^-$	-0.54	-0.54	-1.36
(19)		$SO_4^{2-}(aq) + H_2O(l) + 2e^- \rightleftharpoons SO_3^{2-}(aq) + 2OH-(aq)$	-0.93	n/a	-1.76

(20)	$SO_4{}^{2-}(aq) + 4H^+ + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.12	+0.12	n/a
(21)	$2HSO_4{}^-(aq) \rightleftharpoons S_2O_8{}^{2-}(aq) + 2H^+ + 2e^-$	-2.12	-2.12	n/a
(22)	$S_2O_3{}^{2-}(aq) + 6OH-(aq) \rightleftharpoons 2SO_3{}^{2-}(aq) + 3H_2O(l) + 4e^-$	+0.57	n/a	-0.26
(23)	$2S_2O_3{}^{2-}(aq) \rightleftharpoons S_4O_6{}^{2-}(aq) + 2e^-$	-0.08	-0.08	-0.91
(24)	$NO_2-(aq) + 2OH-(aq) \rightleftharpoons NO_3-(aq) + H_2O(l) + 2e^-$	-0.01	n/a	-0.84
(25)	$2NH_3(aq) + 6OH-(aq) \rightleftharpoons N_2(g) + 3H_2O(l) + 3e^-$	-0.77[27]	n/a	-1.60
(26)	$2NH_4OH(aq) \rightleftharpoons N_2(g) + 2H_2O(l) + 6H^+(aq) + 6e^-$	-0.09	-0.09	n/a
(27)	$2NH_4{}^+(aq) \rightleftharpoons N_2H_5{}^+(aq) + 3H^+(aq) + 2e^-$	-1.28	-1.28	n/a

$$2Cl^-(aq) \rightleftharpoons Cl_2(g) + 2e^- \qquad (-1.36V) \tag{15}$$

$$2Br^-(aq) \rightleftharpoons Br_2(l) + 2e^- \qquad (-1.09V) \tag{16}$$

$$2I^-(aq) \rightleftharpoons I_2(l) + 2e^- \qquad (-0.54V) \tag{17}$$

$$3I^-(aq) \rightleftharpoons I3^-(aq) + 2e^- \qquad (-0.54V) \tag{18}$$

There are a large number of possible competing reactions based on sulphur-containing anions (equations 19 to 23). There are many redox potentials for sulphate ions, but the most competitive is given in equation 20 for an acidic solution , and in equation 20 for basic media. Equation 19 in basic solutions is competitive with water oxidation, but occurs at a less positive potential and so should not dominate. Equation 20 is significantly more positive than water oxidation and so should remove any oxygen production. The competing bisulphate oxidation reaction, equation 21, only occurs in acidic solutions and is 0.79 V less positive than water oxidation.

$$SO_4{}^{2-}(aq) + H_2O(l) + 2e^-$$
$$(-0.93V) \tag{19}$$
$$\rightleftharpoons SO_3{}^{2-}(aq) + 2OH-(aq)$$

$$SO_4{}^{2-}(aq) + 4H^+ + 2e^-$$
$$(+0.12V) \tag{20}$$
$$\rightleftharpoons H_2SO_3(aq) + H_2O(l)$$

$$2HSO_4{}^-(aq) \rightleftharpoons S_2O_8{}^{2-}(aq) + 2H^+(aq) + 2e^- \qquad (-2.12V) \tag{21}$$

$$S_2O_3{}^{2-}(aq) + 6OH-(aq)$$

$$\rightleftharpoons 2SO_3{}^{2-}(aq) + 3H_2O(l) + 4e^-$$ $\qquad$ (+0.57V) $\qquad$ (22)

$$2S_2O_3{}^{2-}(aq) \rightleftharpoons S_4O_6{}^{2-}(aq) + 2e^-$$ $\qquad$ (–0.08V) $\qquad$ (23)
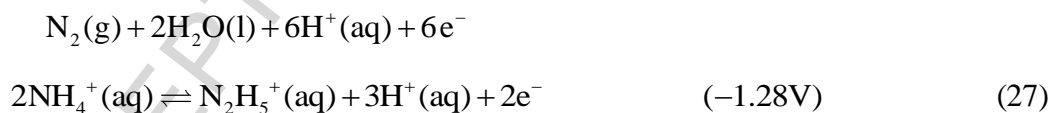
Thiosulphate $(S_2O_3{}^{2-})$ has a very competitive oxidation reaction in basic solutions, in equation 22 which should dominate over water, and another one in equation 23 which would compete in both acidic or basic solutions, but is less positive than equation 22 in basic solutions. Neither of the thiosulphate oxidation reactions produce gases.

$$NO_2-(aq) + 2OH-(aq)$$

$$\rightleftharpoons NO_3-(aq) + H_2O(l) + 2e^-$$ $\qquad$ (–0.01V) $\qquad$ (24)

The nitrite anion is competitive at the positive terminal as well as the negative terminal, as shown in equation 24, producing nitrate anions. This reaction will only proceed in basic solutions, but is very competitive and will probably dominate over water oxidation.

$$2NH_3(aq) + 6OH-(aq) \rightleftharpoons$$

$$N_2(g) + 3H_2O(l) + 3e^-$$ $\qquad$ (–0.77V) $\qquad$ (25)

$$2NH_4OH(aq) \rightleftharpoons$$

$$N_2(g) + 2H_2O(l) + 6H^+(aq) + 6e^-$$ $\qquad$ (–0.09V) $\qquad$ (26)

$$2NH_4{}^+(aq) \rightleftharpoons N_2H_5{}^+(aq) + 3H^+(aq) + 2e^-$$ $\qquad$ (–1.28V) $\qquad$ (27)

The final set of equations are related to ammonium cation ($NH_4{}^+$) oxidation. Equation 25 gives an example of direct oxidation to generate nitrogen gas at a slightly more negative potential than water oxidation (-0.77 V vs -0.40 V), which should occur only in basic solutions. Equation 26 appears to give a corresponding equation for acidic media which is much more competitive, and likely to prevent water oxidation, and again produces nitrogen (although at half the rate of equation 25 per mole of oxidation). The final equation 27 is a solution-based half equation which should only occur in acidic media again, so could compete with previous equation only if the kinetics inhibit equation 26 with its more positive potential (-0.09 V vs -1.28 V). All of these equations are also shown in table 4.

4. Results

A variety of sodium and potassium salts at a fixed concentration of 5 wt% were all compared directly, and the results for these sixteen discharge tests are shown in table 5. The final cell voltage, cell mass, conductivity, pH and specific gravity (SG) are all shown after leaving the fully-charged cell in the solution for 24 hours.

Table 5: Saline solution and battery properties before and after discharge, for all 26 solutes.

	INITIAL				FINAL					
	Conductivity (mS.cm^{-1})	pH	SG	Cell mass (g)	Voltage (V)	Conductivity (mS.cm^{-1})	pH	SG	Cell mass (g)	Δ mass (g)
NaCl	75.9	6.0	1.032	44.78	—^{a}	74.4	7.2	1.030	43.11	-1.67
NaHSO$_4$	86.4	0.9	1.032	44.72	2.57	86.8	1.3	1.033	44.47	-0.36
Na$_2$SO$_4$	43.7	5.1	1.040	44.59	2.77	46.0	7.0	1.040	44.57	-0.02
Na$_2$S$_2$O$_3$	38.4	7.6	1.039	44.65	—^{a}	47.5	8.3	1.037	44.33	-0.32
NaNO$_2$	57.1	7.3	1.030	44.66	1.79	62.3	10.9	1.030	44.66	0.00
NaNO$_3$	48.6	5.2	1.030	44.70	2.45	49.3	9.4	1.030	43.88	-0.82
NaHCO$_3$	33.6	7.7	1.032	44.76	3.26	33.9	8.7	1.030	44.86	0.10
Na$_2$CO$_3$	50.9	11.3	1.047	44.53	2.22	50.1	10.8	1.047	44.60	0.07
Na$_3$C$_6$H$_5$O$_7$	26.8	8.3	1.030	44.70	3.36	27.8	8.3	1.032	44.69	-0.01

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^{a} NH$_3$ molecular weight as NH$_4$OH

NaOH	—[b]	12.9	1.047	44.74	—[c]	—[b]	11.1	1.049	43.05	-1.69
Na₂HPO₄	32.8	8.7	1.043	44.53	3.49	30.3	8.8	1.043	44.63	0.10
NaH₂PO₄	20.5	4.1	1.033	44.60	3.65	22.5	4.6	1.031	44.70	0.10
KCl	67.3	7.6	1.023	44.74	—[a]	71.0	6.6	1.027	42.62	-2.12
KBr	52.4	7.4	1.032	44.75	—[a]	53.3	6.4	1.031	42.68	-2.07
KI	38.0	7.3	1.033	44.79	—[a]	37.7	6.9	1.032	42.88	-1.91
KHCO₃	35.4	8.5	1.027	44.77	2.75	42.8	8.9	1.028	44.70	-0.07
K₂CO₃	65.0	11.8	1.040	44.70	2.00	63.9	11.8	1.040	44.55	-0.15
K₃PO₄	54.4	12.5	1.043	44.80	—[c]	54.5	12.6	1.044	43.23	-1.57
K₂HPO₄	44.2	9.3	1.038	44.68	3.20	44.6	9.1	1.039	44.61	-0.07
KH₂PO₄	26.8	4.3	1.030	44.83	3.63	27.1	4.2	1.032	44.75	-0.08
(NH₄)₂SO₄	58.6	4.9	1.026	44.69	3.27	61.7	6.0	1.025	44.68	-0.01
NH₄HCO₃	38.7	7.7	1.020	44.73	3.13	44.3	8.3	1.015	44.72	-0.01
(NH₄)₂CO₃	53.8	9.0	1.018	44.83	2.28	50.5	9.1	1.015	44.75	-0.07
(NH₄)₂HPO₄	33.8	8.2	1.029	44.70	3.49	42.0	8.2	1.027	44.70	0.00
NH₄H₂PO₄	22.7	4.1	1.02	44.6	3.63	28.7	4.3	1.02	44.6	-0.0

[b] pH too high for conductivity meter

[c] Cathode not visibly corroded

			5	2				3	1	1
NH$_3$	1.07	11.8	0.971	44.72	3.63	1.21	12.3	0.970	44.71	-0.01

4.1. Solution properties

In table 5 pH, conductivity and specific gravity have been measured once before discharge and once at the end. In many cases, particularly the sodium and potassium solutions, there is marginal change in the properties between the beginning and the end unless significant corrosion was observed. Two notable exceptions to this are the sodium nitrate (NaNO$_3$) and sodium nitrite (NaNO$_2$) where the pH jumped up significantly in both cases, perhaps indicating that OH- ions were not oxidised into oxygen at the positive terminal, and that the NO$_3^-$ and NO$_2^-$ ions underwent a significant competing reaction at this terminal.

There are fewer ammonium salts, and so observing trends in these single-test data points is risky, but one distinct trend is that all of them exhibit a reduction in specific gravity, most significantly in ammonium bicarbonate (NH$_4$HCO$_3$ from 1.020 to 1.015). However, this could just reflect significant loss of ammonia gas from a well-dissolved state. Some ammonium solute conductivities seem to change more significantly than for the sodium and potassium solutes, particularly the ammonium phosphates ((NH$_4$)$_2$HPO$_4$ from 33.8 mS.cm^{-1} to 42 mS.cm^{-1}, NH$_4$H$_2$PO$_4$ from 22.7 mS.cm^{-1} to 28.7 mS.cm^{-1}), although the other solutes are probably not beyond a realistic error margin.

The rate of gas production at the electrodes was also qualitatively assessed, but the differences between high and medium gas production are hard to pinpoint. What was more definite was that all the electrodes seemed to produce significant quantities of gas bubbles at the beginning of electrolysis, with the notable exceptions of the negative terminals of cells in NaNO$_3$ and NaNO$_2$ solutions, and both terminals of the cell in NH$_3$.

4.2. Discharge rates

Figure 3 shows the voltage plotted as a function of time for the same discharge experiments. As can be seen in the insets, by 10 hours only the cell in sodium nitrite (NaNO$_2$) has passed below the 3.5 V mark, when the remaining charge capacity drops to below 500 mAh (see figure 2a). However, K$_2$CO$_3$ and NaNO$_3$ are below 3.6 V, and a number of salts are under 3.7 V, most notably

Na_2CO_3 which accelerates between 10 and 24 hours to overtake $NaNO_3$. However, figure 4 shows that the different in voltage at 24 hours is really insignificant in terms of discharge capacity. In terms of energy capacity, this is even less significant, as demonstrated by the differences between figures 2a and 2b.

The positive terminals of the cells in the halide solutions (NaCl, KCl, KBr, and KI) and the thiosulphate ($Na_2S_2O_3$) corrode fast, and they all barely last the first hour before a stable voltage cannot be measured (and the probing probes further damage the terminals during measurement).

The cell in NaOH solution appears to last no longer than those in the the halide solutions, before the voltage falls negative (unstable at ≈ -0.2 V), whilst K_3PO_4 lasts beyond 10 hours before it gives no stable final 24 hour voltage (table 5).

Table 5 gives some clues as to why NaOH and K_3PO_4 might have this problem, where their final cell masses are considerably lower than their initial ones (3.8 % lower for NaOH, and 3.5 % for K_3PO_4). Additionally, the solutions both appeared to give off the sweet scent of the polycarbonate ester solvents from within the cells, indicating that some electrolyte solution has leaked into the aqueous solutions. The NaOH pH is significantly reduced to 11.1 after discharge from the initial value of 12.9, but the K_3PO_4 pH is not reduced at all.

After the $NaNO_2$ and $NaNO_3$ the 5 wt% CO_3^{2-} solutions clearly discharge the cells fastest according to figure 3. Nevertheless, the HCO_3^-, SO_4^{2-} and HPO_4^{2-} solutions come steadily behind for more than one cation, which could just be down to lower conductivities of these solutes. Figure 4 shows that this is partly true in some cases, although solubility limits of salts like NaHCO3 and Na_2HPO_4 mean that conductivities above 100 mS.cm^{-1} might be impossible to achieve for solutions of these salts.

Below the chart in figure 4 the conductivities of all the solutions are given in three different lines. The top line refers to solutions with particularly high discharge at 10 hours after commencing discharge, the bottom line refers to those at a fairly standard rate (or particularly low one), and the middle one partly accommodates slightly higher than standard discharge rates, or those that are fully corroded by 10 hours. As well as sodium nitrite and nitrate, sodium citrate ($Na_3C_6H_5O_7$) and ammonia (NH_3 or NH_4OH) shows noticeably fast discharge for their measured conductivity than others. Whilst sodium sulphate also partly does, the two different measurements made for sodium sulphate are included to highlight that the same solution could give quite different capacity results when reproduced, even though the precise voltages were not very

different (3.65 V vs 3.62 V), the capacity these voltages corresponded to at that point was over 100 mAh apart.

Pure ammonia solution showed very odd discharge kinetics, particularly given that a 5 wt% solution has a conductivity of only ≈ 1 mS.cm^{-1}. Discharge appeared to start very slowly and then accelerate after 5 hours, overtaking three solutions with conductivities over 20 mS.cm^{-1} by 24 hours to reach almost 65 % total discharge (3.63 V). Accounting for these variations in kinetics is hard to pick out, but an important consideration is the potential window of the redox reactions taking place at the electrodes. Water has a potential window of 1.23 V, and any solutes which have reactions that reduce this window may manage to speed up the relative discharge at lower voltages versus those that just undergo water electrolysis. Possible competing reactions have been explored in the discussion, in section 3.

4.3. Corrosion

In the supplementary information a photo shows most of the Na$^+$ and K$^+$ solutions with cells in them approximately 10 minutes after starting the experiments. This shows how rapidly the steel corrosion by the halide solutions occurs versus the rest, with the exception of sodium thiosulphate, also shown in a separate photo in the supplementary information.

Figure 5 shows the corrosion of a cell in NaCl solution after 5, 10, and 24 hours. The part that corrodes the most, the positive terminal, is shown on the left. The negative terminal in the middle shows some red iron (III) oxide, although how much is corrosion on the terminal itself and how much adsorbed particles is not clear. The image of the 2 litre vessel shows how full of this corroded material the aqueous solution was, and also shows how the particles settled over the 24 hour period, although this probably just reflects a reduction in gas formation as electrolysis reduces. Within a minute of discharge commencing in the two litre, 5 wt% NaCl solution, red corrosive products were being formed, and these images highlight how corrosive NaCl is.

With the cylindrical LIB cells, most corrosion occurs at the high voltage positive terminal, and so a matrix of positive terminal photos is shown in figure 6, demonstrating the visual corrosion for all 26 solutes at 5, 10, and 24 hours after starting the experiments. The negative terminals are shown in the supplementary information in a similar manner.

Aside from the rapid corrosion by NaCl, $Na_2S_2O_3$, KCl, KBr, and KI solutions, a couple of other clear features can be observed from figure 6: a number of cells exhibit blackening of the

terminal during discharge (and in some cases this clears up by 24 hours), the terminal falls off in acidic sodium bisulphate ($NaHSO_4$), many terminals have small signs of iron (III) oxide by 24 hours, and the blue insulating paper is variously damaged in different salts. In some cases the photo was taken while the cell was still wet meaning that the cell looks shiny, and in some cases, only really at 24 hours though, the cell dried without being wiped and so some salt deposits can be seen on the cell.

Unfortunately, with the exception of ammonium bicarbonate (NH_4HCO_3) particularly non-hazardous, mildly alkaline salts comprising of bicarbonate (HCO_3^-) or monohydrogen phosphate (HPO_4^{2-}) anions all seem to cause some form of black deposit on the positive terminal. Whilst this could be a deposit and not any significant corrosion, it is not that positive for future use of the cell. Indeed, the dihydrogen phosphates ($H_2PO_4^-$) seem to demonstrate less corrosion despite their acidic pH.

Figure 6 shows some unexpected results, such as lower corrosion on cells in higher alkalinity K_2CO_3 vs Na_2CO_3, and no visible major corrosion on some cells where significant mass was lost, those discharged in NaOH, $NaNO_3$, and K_3PO_4. There are also a number which show virtually no rusting, and others than show clear levels of rusting. These experiments show single runs, and fully conclusive results will require multiple tests, but they give good starting points for understanding what will definitely cause corrosion, and those which are likely to cause minor corrosion at worst.

4.3.1. Impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was done on the cells where sufficient contact could be made at both terminals (so visible corrosion was ok as long as it had not removed the terminal completely). The cells which had lost significant levels of mass generally showed very irregular impedance measurements (and sometimes errors in the measurement), and so are not included here. Those with unstable EIS measurements included the cell discharged in sodium bisulphate ($NaHSO_4$) solution, despite giving a (supposedly) stable voltage reading after 24 hours discharge.

For comparison, EIS measurements were carried out on pristine cells at different voltages on discharge from fully charged at 4.2V. The Nyquist plot of impedance, showing imaginary (vertical) and real (horizontal) components of impedance, is shown in figure 7. The pristine cell

measurements are shown in different colours from 1.33 V up to 4.21 V, and the cells discharged in different solutions are shown in dark solid curves with labels outlining the solute and the 24 hour measured voltage.

All of the cells seem to plot roughly where would be expected given their final measured voltage, with the notable exception of ammonia (NH_3). With a conductivity of only 1 mS.cm^{-1}, the fact the NH3 discharged to 3.63 V was unexpected, but the EIS measurement would place the final Nyquist plot resistance as typical of a cell between 3.13 V and 2.92 V.

5. Discussion

As mentioned in the introduction, the vast majority of previously reported studies on aqueous solution discharge use NaCl solution [5, 6, 7, 9, 11, 13, 14], which might explain the relatively low interest in this process for cell discharge. Amongst the other academic studies, only three give specifically different solutes for solution discharge: Nie et al. [10] used a saturated Na_2SO_4 solution with iron powder, for 24 hours, Li et al. [16] used Na_2SO_4, and Ojanen et al. [17] used $NaSO_4$ (sic), $FeSO_4$, $ZnSO_4$, as well as NaCl. All the other studies were less specific, referring either to 'brine' [4, 12], which could imply sea-water composition, or unspecified electrolytic solutions [8, 15].

5.1. Solution properties

Table 5 shows the range of solution pH's, and the mass change result for the only solution with a pH < 4 ($NaHSO_4$) demonstrates that the steel casing is vulnerable to acidic solutions. The nickel-plated steel top of the positive terminal dropped off within five hours. Although a stable voltage for the cell in $NaHSO_4$ could still be measured after 24 hours, a significant mass loss was observed (almost 1 %), and no stable EIS measurement was observed, hence its absence from figure 7.

The drop in masses for highly alkaline solutions (pH > 12) shows that high pH's are also risky for corrosive results. Given that Na_2CO_3 and K_2CO_3 both give 5 wt% solution pH above 11, it is not surprising that some discharge events with these salts possibly perforated the can. The general conclusion has to be that moderate pH's are desirable to be certain of avoiding can penetration due to H^+ or OH^- ions, although if the damage is only due to gasket corrosion, this is

much less likely to be a risk for pouch cells.

Given that both the rate of discharge should be strongly linked to conductivity, and corrosion should be at least partly influenced by the rate of discharge, solution conductivity was measured. Conductivity depends strongly on the ionic nature of the compound dissolved in the solution, and the corresponding ability of it to dissociate into charged ions, in order to then carry charge. If all the solutes were the salts of string acids and bases we could expect the conductivity to scale directly with molarity, but not all our solutes are the products of strong acids and bases. As table 6 shows, theoretical conductivity also varies depending on the chemistry of the solute itself.

The theoretical conductivity values for 5 wt% solutions are shown in table 6, and the deviation of the measured value from the theoretical value is given as a fraction in the term α (fraction dissociated), with most α values falling between 0.3 and 0.8. The notable (and only) exceptions are NaHSO$_4$, which showed a considerably higher ($\alpha = 1.93$) measured conductivity than the theoretical value, and NH3 which was significantly lower ($\alpha = 0.0025$).

Table 6: Sodium, potassium and ammonium ionic solutes used in these experiments.

	NaCl	Na$_2$SO$_4$	NaNO$_3$	NaHCO$_3$	Na$_2$CO$_3$	NaOH	Na$_2$HPO$_4$	NaH$_2$PO$_4$	NaHSO$_4$	Na$_2$S$_2$O$_3$	NaNO$_2$	Na$_3$C$_6$H$_5$O$_7$
Molecular weight	58.440	142.036	84.994	84.006	105.988	39.997	141.958	119.976	120.054	158.097	68.995	258.069
5 wt% solution molality	0.90	0.37	0.62	0.63	0.50	1.32	0.37	0.44	0.44	0.33	0.76	0.20
5 wt% solution molarity	0.87	0.36	0.60	0.61	0.47	1.26	0.36	0.43	0.43	0.32	0.74	0.20
5 wt% solution conductivity	75.9	45.4	49.0	33.6	50.9	?	32.8	20.5	86.4	38.4	57.1	26.8

(mS.cm^{-1})												
5 wt% molar conductivity Λ (S.cm^2.mol^{-1})	87.0	127.4	81.5	55.3	107.3	n/a	92.3	48.3	197.1	115.3	74.9	131.4
***Theoretical* molar conductivity Λ (S.cm^2.mol^{-1})**	126.4	260.2	121.5	94.6	238.8	248.1	214.2	86.1	102.1	270.2	172.0	360.8
5 wt% solution fraction dissociated α	0.69	0.49	0.67	0.59	0.45	n/a	0.43	0.56	1.93	0.43	0.44	0.36

	KCl	KBr	KI	KHCO$_3$	K$_2$CO$_3$	K$_3$PO$_4$	K$_2$HPO$_4$	KH$_2$PO$_4$
Molecular weight	74.548	119.002	166.002	100.114	138.204	212.264	174.174	136.084
5 wt% solution molality	0.71	0.44	0.32	0.53	0.38	0.25	0.30	0.39
5 wt% solution molarity	0.69	0.43	0.31	0.51	0.37	0.24	0.29	0.38
5 wt% solution	67.3	52.4	38.0	35.4	65.0	54.4	44.2	26.8

conductivity (mS.cm^{-1})								
5 wt% molar conductivity Λ (S.cm^2.mol^{-1})	95.3	118.5	119.9	69.2	177.5	219.4	146.3	69.3
Theoretical molar conductivity Λ (S.cm^2.mol^{-1})	149.8	151.6	150.3	118.0	285.6	498.8	261.0	109.5
5 wt% solution fraction dissociated α	0.64	0.78	0.80	0.59	0.62	0.44	0.56	0.63

	(NH$_4$)$_2$SO$_4$	(NH$_4$)$_2$HPO$_4$	NH$_4$H$_2$PO$_4$	NH$_4$HCO$_3$	(NH$_4$)$_2$CO$_3$	NH$_3$
Molecular weight	132.134	132.056	115.025	79.055	96.086	35.046[a]
5 wt% solution molality	0.40	0.40	0.46	0.67	0.55	1.50
5 wt% solution molarity	0.39	0.39	0.45	0.65	0.54	1.55
5 wt% solution conductivity (mS.cm^{-1})	58.6	33.8	22.7	38.7	53.8	1.02
5 wt% molar conductivity Λ (S.cm^2.mol^{-1})	147.1	84.8	49.6	58.1	98.2	0.68
Theoretical	307.0	261.0	109.5	118.0	285.6	271.5

[a] NH$_3$ molecular weight as NH$_4$OH

molar conductivity Λ ($S.cm^2 .mol^{-1}$)						
5 wt% solution fraction dissociated α	0.48	0.45	0.32	0.49	0.34	0.0025

The specific gravity values shown in table 5 hardly vary at all during the electrolysis of one 2 Ah cell in 2 litres of solution. Even those which apparently do (e.g. KCl, NH_4HCO_3) are possibly still within the bounds of error given the coarseness of the tool used to measure this. The main reason it has been included is that it is a very practical way for getting a quick solution measurement for any upscaled discharging process. For a given solute, specific gravity is a decent proxy of the concentration, and hence a useful measure of how much the electrolyte has been consumed or contaminated through the electrolysis.

5.2. *Discharge rate*

Discharge rates are critical to any discharge process, and the general aim for any discharge process would be for it to be slow enough to be safe, but not so slow that it becomes a very costly process. For the 18650 cylindrical cells in this study, when they are in a solution on their own, as long as their polymer coating has not been perforated, the shortest path-length for ionic transport of charge between the terminals is roughly 65 mm. When looking at conductivity measurements in $mS.cm^{-1}$, to convert it into resistance we could use the following equation:

$$Resistance\ (\Omega) = 1000 \left(\frac{mS}{S} \right) \times \frac{Ionic\ Path\ Length\ (cm)}{Conductivity\ (mS.cm^{-1}) \times k\ (cm^2)} \tag{28}$$

For the Oakten Cond 6+ device used in this study the cell constant, k, equals 1 cm^2. However the path for the ionic transport between the 18650 terminals is not limited in the same way, meaning that k could well be larger than 1, reducing the overall resistance.

Whilst it may appear that quite large effective solution resistances are obtained; for $k = 1$ and $length = 6.5$ cm these would vary from $87\,\Omega$ at 75 $mS.cm^{-1}$ to $325\,\Omega$ at 20 $mS.cm^{-1}$ (or even $6500\,\Omega$ at 1 $mS.cm^{-1}$). As mentioned before, k is likely to be significantly greater than 1, but it is clear that the solution conductivity is a limiting factor to achieving faster discharge rates,

and the likelihood of a dangerous short-circuit causing thermal runaway is negligible without a significant reduction in the final solution resistance (for the cells used in this study they are rated up to 5C, which means a discharge current of 10 A, or a resistance of $0.42\,\Omega$).

The ionic transport path lengths will be shorter for some pouch and prismatic cells (by the nature of how close together the tabs are), but could be longer for others. The path length could be shortened for cylindrical cells by deliberately damaging the plastic coating. Multiple cells could be stacked in the same bath to reduce the path lengths between terminals, but if this was not done in a controlled manner then the rate of discharge of the cells in the bath could vary significantly.

There are not many studies that have clearly recorded discharge rates for solution discharge. For NaCl, probably the most detailed study is by Li et al.(2016) [13], where 18650s were discharged in different concentrations (5, 10 and 20 wt%) of sodium chloride solution. The initial voltage is not stated, but given that the maximum 'discharge efficiency' (percentage dropped from initial voltage) is $\approx 75\,\%$, which must be around 1.23V, then the likely initial voltage is $1.23 \div 0.25 = 4.92V$. This is obviously unrealistically high, but suggests that the cells were originally fully charged, although given that the discharge went on for 24 hours, and the results were measured manually with a voltmeter, our experience would suggest that any voltage measurements of 18650s discharging in NaCl solutions of 5 wt% or higher for longer than an a couple of hours are likely to be quite unreliable due to corrosion. The 18650s also were of unspecified capacity, so a direct comparison of discharge rate is not really possible. Indeed, Li et al. used a much smaller volume of solution, and so the corrosion might increase the conductivity of the solution, perhaps increasing discharge and associated corrosion rates.

Ojanen et al. [17] carried out most of their cell discharge experiments in a different manner, where the cell was not in the solution but soldered platinum cables were used. For sodium sulphate, which could be compared to the results in this study, more corrosive electrolytic behaviour was observed despite good Pt catalysis of water electrolysis, reducing the half-cell overpotentials. However, there is some doubt about the sodium sulphate chemical formula in their study. Ojanenen et al. did not specify the distance between their Pt wire electrodes, and indeed their photos suggest an uncontrolled distance. They also used a much smaller capacity battery (700 mA Nokia phone cell), and so their discharge rates of minimum 10 hours for 5 wt% solutions compare unfavourably with the times presented in this study, where the discharge time was similar, but for around three times the capacity.

A final study to compare with is Lu et al. [5], who looked at discharge in NaCl solutions with times of around 30 minutes for 5 wt% solutions, but the starting state-of-charge was declared o be 60 %, or ≈ 3.85 V. The capacity of these cells is not clear, nor is the method of determining the voltage, making any comparison difficult.

With so many missing parameters, direct comparisons are impossible, but rapid discharging of large capacities cannot be expected without additional engineering, or significant increases in solution conductivity.

5.3. Corrosion

Corrosion is probably the main consideration during discussions about using aqueous solutions for cell discharge. In some cases rapid corrosion is desired in order to destroy the cell, but in most cases slow corrosion is desired to allow for maximum discharge, allowing safe transportation of undamaged cells, perhaps for reuse, but normally for disposal and materials reclamation.

As mentioned in the results section, the alkaline solutions above a pH of 12 appeared to penetrate the can without visible terminal corrosion. Curiously, table 5 shows that the NaOH pH drops to well below 12 by 24 hours of cell discharge, and yet K_3PO_4 which also starts with a pH of above 12 and appears to penetrate the can, exhibits no drop in pH. This may reflect the length of time that the electrolyte solvent leaking out of the can for, as the cell appears to be compromised after only 2 hours in 5 wt% NaOH solution, but does not cause any irregularities in 5 wt% K_3PO_4 solution until after 10 hours (and possibly not until up to 24 hours). Another explanation could be that the phosphate anion competes with hydroxyl oxidation at the positive terminal, meaning that OH^- ions are not consumed during electrolysis as they would necessarily be for NaOH solutions.

The halides and sodium thiosulphate ($Na_2S_2O_3$) exhibit significant destruction to the positive terminal, and therefore appear to be suitable for cell destruction like the alkaline solutions, although the residue will be much more dirty than one that, presumably, does not corrode the steel but corrodes through the much smaller rubber gasket. Nevertheless, in either case electrolyte solution will leak into the aqueous solution to create a contaminated liquid waste, but a much more containing waste than the way in which damaged cells are standardly stabilised at the University of Warwick: short-circuiting in a protected room, usually by some form of penetration. Even if a short-circuited cell does not burst into flames, electrolyte and gas (if there is any charge to be removed) will escape into the room in a relatively uncontrolled manner.

As mentioned before, the most acidic solution is sodium bisulphate ($NaHSO_4$), and it shows considerable damage to the steel positive terminal, in a cleaner but considerably slower manner than the halides and $Na_2S_2O_3$. Mildly acidic solutions, like the monobasic phosphates (NaH_2PO_4, KH_2PO_4, and $NH_4H_2PO_4$), demonstrate very clean discharge at the positive electrode, but this perhaps suggests that some very slow acidic corrosion is taking place. In figure 6, these mildly acidic solutions cause less visible corrosion to the terminals than mildly alkaline solutions (like the dibasic phosphates, or carbonates). Also, for some cells the rusting was less visible immediately after being removed from the solution compared with after they had dried.

EIS showed that most cells with no weight-loss exhibited inductance and conductance behaviour along the lines of what would be expected from resistively-discharged cells. The only exception to this was ammonia (NH3) which exhibited a Nyquist curve more along the lines of < 3.1 V when the final measured voltage was 3.63 V. Whilst exceptionally odd, this only adds to the confusing pattern of discharge that NH3 solution exhibited, suggesting that more in-depth research into NH3 electrolysis (using Ni-plated steel electrodes) could be considerably more complex than for other aqueous solutes.

The mild effects of corrosion are not really necessary to quantify for cell disposal, as the main finding that corrosion rates are considerably slower than discharge rates for most solutes will satisfy this requirement. However if there is any intention to re-use the cell then the choice of solutes will have to be examined more closely to ensure that any mild corrosion will not have longer-term effects on cell performance and safety.

Previous literature has also observed corrosion at steel terminals with NaCl solutions, which is why Ojanen et al. [17] used platinum wires to remove electrode corrosion, although Lu et al. [5] suggested that low concentration solutions (1 wt%) could reduce the corrosion whilst still discharging the cells. Nevertheless, the problems associated with comparing previous literature results due to a lack of recorded details, outlined in the previous subsection on discharge rates, still apply for corrosion rates.

5.4. Fire hazards

When considering electrolysis of water, the generation of hydrogen is particularly dangerous, especially because of the mutual generation of oxygen means that the creating an inert environment is difficult. Nevertheless, the hydrogen will not spontaneously combust unless there

is at least 4 vol% of H_2 in the gaseous mix [28]. 4 % represents the lower limit for upward propagation of a flame through the mixture; for horizontal propagation this limit rises to 6%, and for downwards propagation it is as high as 9 %. This is nearly irrelevant of the oxygen concentration (so long as there is oxygen for combustion). Kumar [28] showed that upward propagation of the flame through a hydrogen gaseous mixture shows weak or no dependence on diluent type or concentration, whereas downwards propagation did show relatively significant variation depending on gas type. Given the need to be conservative with health and safety, a strict upper limit of 4 % H_2 must be observed to ensure safety, which will require a good ventilation system.

The generation of alternative gases to hydrogen or oxygen is interesting, but some gas analysis must be carried out before speculating about specific hazards associated with any of them. Although it may be thought that the use of ammonium solutes might reduce hydrogen generation at the negative terminal from water electrolysis, they still were seen to produce gas at both terminals, and although ammonia could in theory be produced at the negative terminal [29], it is still a gas. That said, ammonia is less flammable than and more soluble than hydrogen. Nitrogen gas could also then be generated from electrolysis of ammonia at the negative terminal [30].

5.5. *General observations*

This study is a systematic academic analysis of an applied topic, but with it being such an applied topic there is a desire to make some applied recommendations and generalisations.

A single type of cylindrical cell has been analysed in this study, and the limiting factors have been the positive terminal, whose geometry will vary to a certain extent between models, and the gasket, which could be made of different materials, but needs to be insoluble and non-reactive to the electrolyte solution. The level of variation between models is unlikely to have a significant effect on the discharge properties in solutions as demonstrated in this article. The geometry of cylindrical Li-ion cells is relatively well standardized to 18650s, although larger 26650 and 21700 geometries, amongst others, are possibly reducing the level of cylindrical standardisation. These should not have a big effect on discharge characteristics either, except prolonging the discharge due to greater capacity.

Intact polymer wrapping appears important to prevent a shorter path between the terminals (otherwise the discharge could be much quicker), and an additional step in the discharge process

could be shortening the path by cutting into the polymer wrapping.

Other geometries will vary according to the packaging materials. Pouch cells with polymer aluminium laminate packaging are likely to be relatively inert to most aqueous solutions, unless considerably acidic or alkaline, but this could cause catastrophic penetration if the polymer layer is removed too rapidly. Pouch cell terminals are normally Ni-plated, and therefore should generally show similar patterns for corrosion as observed in the 18650 cells in this study, but they could be made of different metals, particularly copper or aluminium which may corrode at different rates. The terminals are also possibly closer to each other than for cylindrical cells (some with larger capacities), so some degree of care will be required to ensure safe discharge of pouch cells in aqueous solutions.

Prismatic cells vary quite a lot, but most are steel-cased, meaning that the same sort of corrosion may be expected to be observed, but there will also be polymer wrapping and different terminal path lengths to consider. Due to the variability in prismatic geometries, this is probably the hardest to draw general conclusions, but for any cell type, immersion in relatively low-concentration inert solute would seem advisable. A solution of bisodium phosphate (Na_2HPO_4) or sodium bicarbonate ($NaHCO_3$) would seem safe places to start, particularly since they are not highly soluble.

With respect to solute choice, this will depend on the requirement of the discharger, but for non-corrosive discharge it appears that there are a wide range of options with weak anions (carbonates, phosphates), although use of sodium nitrite appeared particularly attractive for fast and low-corrosion discharge. Perhaps a mixture of solutes may be desired for optimal performance in different scenarios, to optimise the discharge characteristics with the price of the solution (and waste disposal), and also perhaps minimise environmental impacts as far as possible.

For destroying damaged cells, a corrosive solution would be desirable. NaCl is an obvious choice given its abundance, but neater options may include those that target the rubber gasket alone, such as alkaline agents like NaOH or K_3PO_4, although these could result in a less reliable passivation of the cell interior than a solution that could attack the metallic casing, like a stronger acid. However, ensuring that the solution will remove HF - the most dangerous product of electrolyte-water reaction - might indicate that an alkaline solution would be preferable, but alternative HF-scavenging agents could also be used. As is often the case, a combination of solutes may the optimal solution when destroying a cell with aqueous solutions.

6.   Conclusions

This study has presented evidence on the effectiveness of aqueous electrolyte solutions for discharging a single type of lithium-ion battery cell in a systematic way. Nickel-plated steel cylindrical cells are a relatively common form, and the capacity of ~ 2 Ah, although low compared with even some large cylindrical cells, is reasonable for estimating how long larger capacity cells may take to discharge in solutions of the same conductivity.

The evidence shows that electrolytic discharge has the potential to be a flexible and safe way to stabilise a wide range of different types of high-energy cells. The rate of discharge will vary depending on a number of factors, but primarily on the actually solution resistance - itself depending on both the conductivity of the medium and the distance between the electrodes. The rate also appears to depend strongly on the chemistry, and presumably the competing electrolytic reactions, but unless very concentrated solutions are used it appears that the rate will always be relatively constrained, and the risk of short circuit low.

For the range of solutes tested here, a huge range of different corrosive behaviours have been observed from almost no corrosion at all to complete destruction of the positive terminal. Although the low-hazard mildly alkaline bicarbonates (HCO_3^-), and the dibasic hydrogen phosphates (HPO_4^-) discharged fine, only the cell discharged in ammonium bicarbonate (NH_4HCO_3) did not show any dark residue on it's positive terminal. Indeed the non-hazardous mildly acidic monobasic hydrogen phosphates ($H_2PO_4^-$) exhibited uniform corrosion-free terminals. Amongst the other solutes, the rate of discharge of the sodium nitrite ($NaNO_2$) solution makes nitrites particularly interesting, despite their human toxicity, because nitrites are notably non-corrosive to steels.

From a practical perspective, the choice of solute will depend on whether the purpose of stabilisation is to destroy the cell completely, or to simply discharge the cell to a safe level with minimal damage. If someone would like to destroy the cell safely using a solution process, then they will end up with a toxic liquid waste because the leaked electrolyte will react with the water to create HF. If they want to discharge a cell with minimal corrosion, then this is possible for the standard nickel-plated steel cells tested here, but a careful choice of a non-corrosive solute for the specific cells to be discharged is essential to achieve this.

A second consideration may be how fast the process will take, and certain solutes will not be soluble enough to reach desired conductivities. For refining solution choices a number of factors will come into play including cost, availability, and health, safety & environment (HSE) impacts. Although not showing the electrolysis product hazards, the hazard list in table 2 shows the official hazard labels assigned to the solutes used here.

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Figure 1: Breakdown of the components of a typical Sanyo UR18650RX by weight, total is 44.62 g.

Figure 2: Capacity-Voltage curves depicting the charge capacity (a) and energy capacity (b) as a function of voltage. For the charge capacity (a), the gradient is also shown. For the energy capacity (b), a logarithmic plot is also shown depicting the energy capacity as a proportion of the maximum capacity.

Figure 3: The cell voltage as a function of time for all 26 solutes; for each plot a close-up of the time period between 0 and 10 hours is shown in the insets. The graph is shown split into the solutes with the three different cations to try and make it easier to pick out the individual salts.

Figure 4: Total discharge capacity as a function of conductivity at various time-points after commencing discharge. The different solutes and their initial conductivities are given below the plot, and are aligned to correlate approximately with the rate of discharge (high level = high rate, low level = low rate and medium = medium or corroded). The dashed lines are just to guide the eye to those that have discharged to a high or low level after 10 hours.

Figure 5: The positive and negative terminals, and the NaCl solution at different times after discharging the cell in the NaCl solution.

Figure 6: Images of the positive terminals after immersion in all 26 different solutions at 5, 10 and 24 hours of discharge in 5 wt% solutions.

Figure 7: Nyquist plot of the (undamaged) discharged cells compared with pristine cells, simply fully charged to 4.2 V and then discharged to different voltages before electrical impedance

spectroscopy (EIS) is carried out between 100kHz and 10mHz.

Graphical abstract

Aqueous solution discharge of cylindrical lithium-ion cells

Highlights:

- Different solutions have very different rates of discharge and corrosion
- Some commonly available non-toxic solutes, namely bicarbonates and hydrogen phosphates, give very low-corrosion discharge
- Other very common solutes, particularly halides such as NaCl, cause devastating corrosion to the positive terminal in a matter of minutes
- Solutes with redox reactions that compete with water electrolysis may cause faster discharge, as demonstrated by $NaNO_2$, a low corrosion yet fast discharge salt
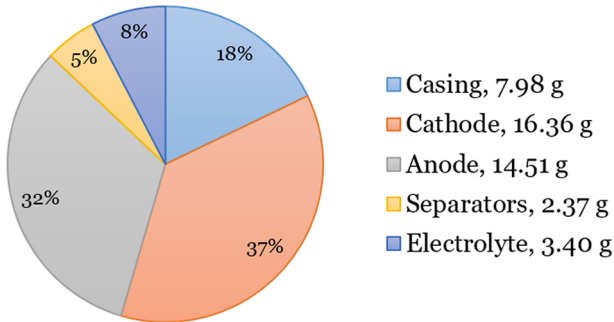
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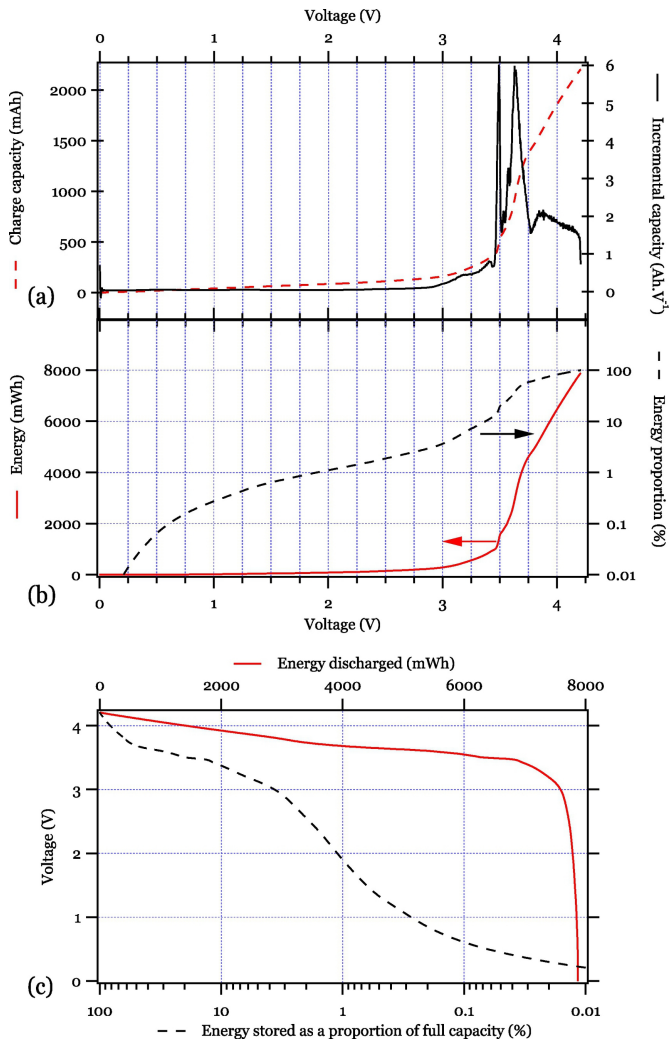
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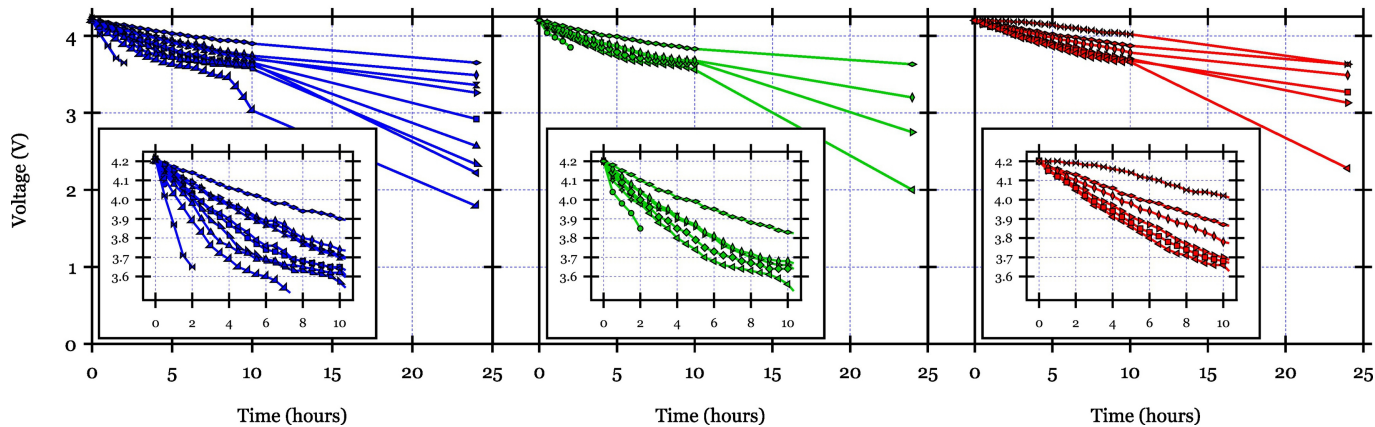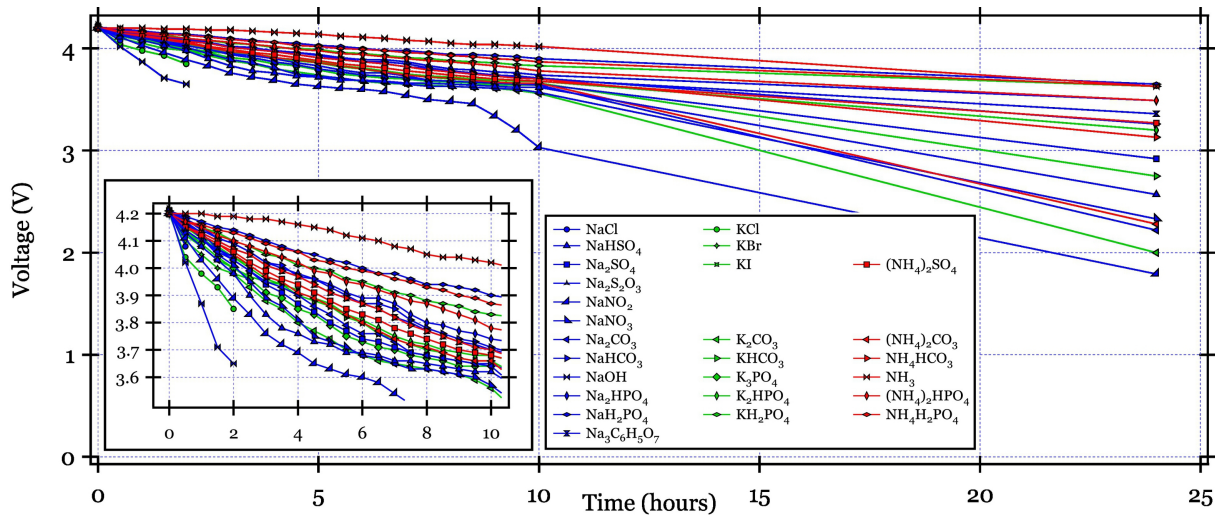
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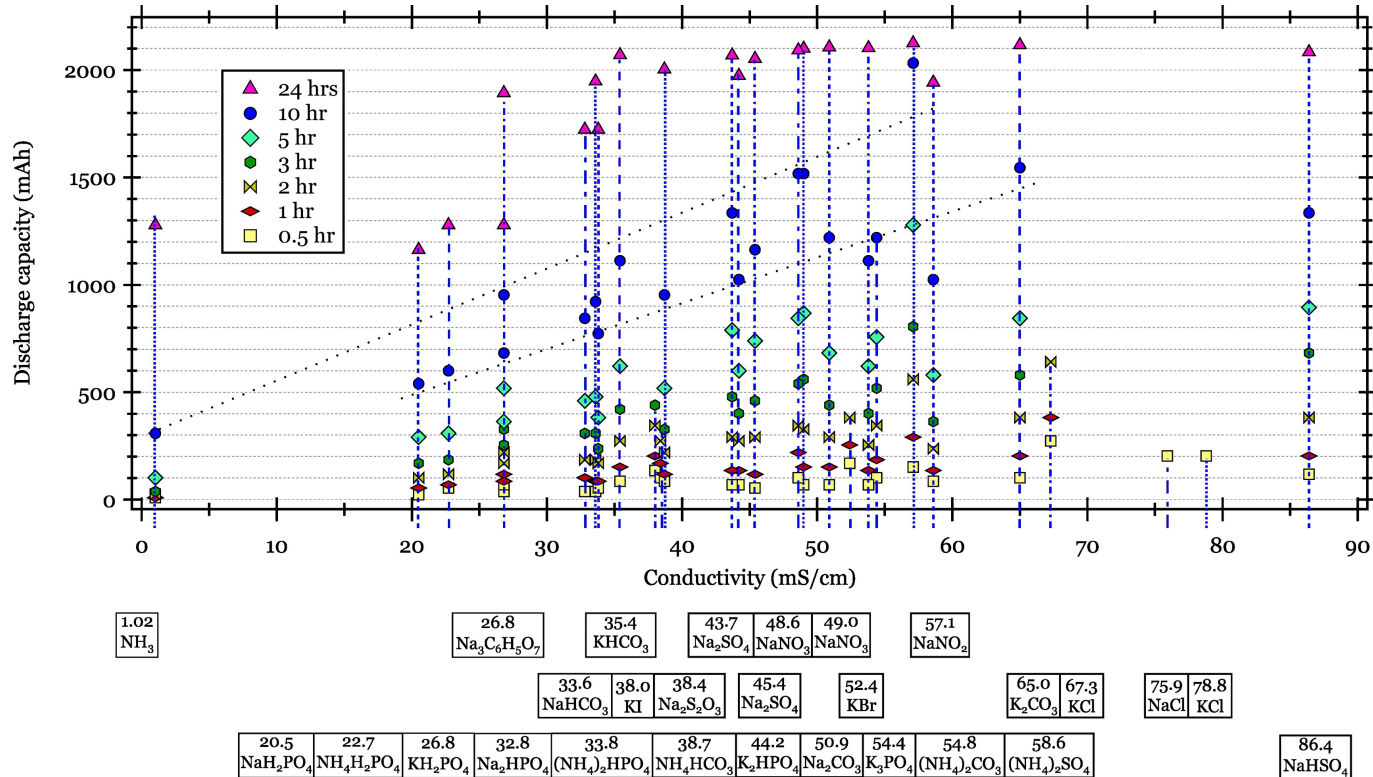
Legend:
- NaCl
- NaHSO$_4$
- Na$_2$SO$_4$
- Na$_2$S$_2$O$_3$
- NaNO$_2$
- NaNO$_3$
- Na$_2$CO$_3$
- NaHCO$_3$
- NaOH
- Na$_2$HPO$_4$
- NaH$_2$PO$_4$
- Na$_3$C$_6$H$_5$O$_7$
- KCl
- KBr
- KI
- K$_2$CO$_3$
- KHCO$_3$
- K$_3$PO$_4$
- K$_2$HPO$_4$
- KH$_2$PO$_4$
- (NH$_4$)SO$_4$
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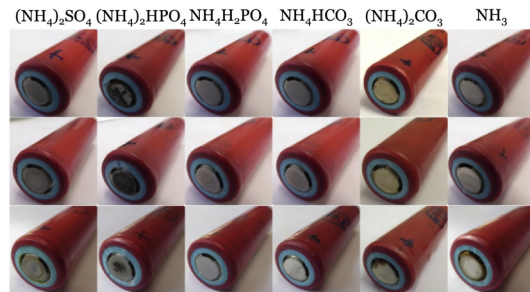- NH$_4$H$_2$PO$_4$
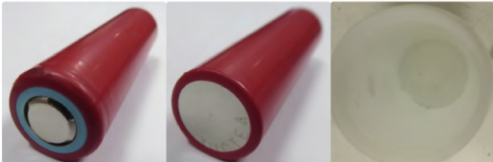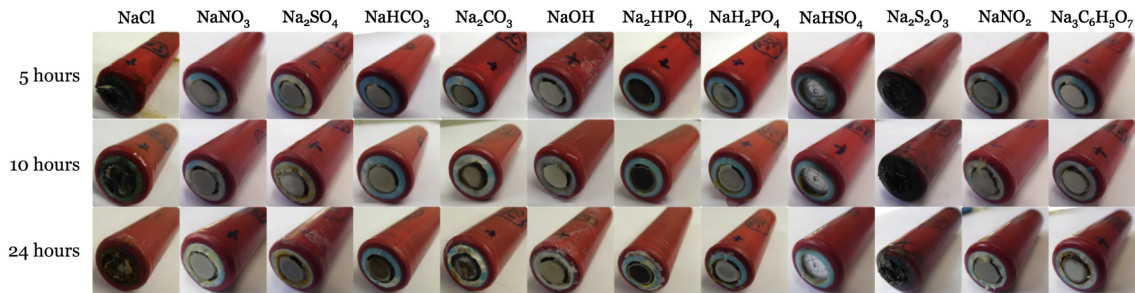
Figure 4

Figure 5
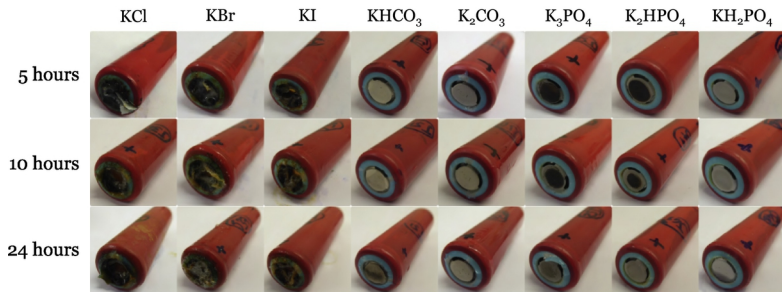
(a) Na$^+$ solutions

(b) K$^+$ solutions

(c) NH$_4^+$ solutions

Figure 6

Figure 7